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NUCLEAR-MAGNETIC-RESONANCE RELAXATION BY SPIN-ROTATIONAL INTERACTIONS IN THE SOLID

R. Blinc and G. Lahajnar
Nuclear Institute "J. Stefan," University of Ljubljana, Ljubljana, Yugoslavia

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The interaction of the nuclear magnetic dipole moment with the magnetic field produced by rotation of the molecule containing the nucleus is known to operate in gases and the modulation of this interaction by molecular collisions is in many cases rate determining for nmr relaxation. Until a few years ago, however, it was generally assumed[1] that anisotropic interactions completely quench the molecular rotational magnetic moment in the condensed phases and that spin-rotational interactions therefore vanish both in liquids and in solids. Gutowsky[2] was the first to point out that this is not always the case for liquids[3,4] and that spin-rotational interactions in some fluoromethanes significantly contribute to the nuclear magnetic relaxation. In the present Letter we report what we believe is the first experimental evidence that spin-rotational interactions do operate in some molecular solids and represent in a certain temperature range the dominant nmr spin-lattice relaxation mechanism.

The temperature dependences of the F^{19} spin-lattice relaxation times (T_1) of SF_6, SeF_6, and TeF_6, observed at 9.2, 15.2, and 23.1 Mc/sec by pulse methods, are presented in Fig. 1 and show, except at very low temperatures, the same anomalous behavior as found by Gutowsky[4] and Hubbard[5] to be characteristic for the presence of spin-rotational interactions. Three different T_1 regions are apparent: the liquid (above −51°C for SF_6, −35°C for SeF_6, and −38°C for TeF_6), the solid phase I (between the melting point and −182°C for SF_6, −146°C for SeF_6, and −72°C for TeF_6), and the low-temperature solid phase II. Second-moment data demonstrate a high degree of reorientational freedom in the solid phase I: The intramolecular dipolar interactions are averaged out and only the intermolecular interactions contribute to the observed F^{19} second moments. Linewidth transitions in SeF_6 and TeF_6 at −150°C and −110°C, respectively, demonstrate the freezing in of this motion in solid phase II.

In liquid SF_6 the T_1 results agree with the ones of Hubbard and Hackleman[6]: Here as well as in SeF_6 and TeF_6 the relaxation times are frequency independent and slowly increase with decreasing T, demonstrating that spin-rotational interactions are dominant.[6] The interesting thing is, however, that this trend is still preserved in the solid phase I even more than 100° below the melting point. After a small initial drop on going from the liquid to the solid, the relaxation times <u>increase</u> with <u>decreasing</u> temperature until in SeF_6 and SF_6 a flat maximum is reached. In SeF_6 the flat plateau extends till the solid-solid transition point dividing phase I from phase II, whereas in SF_6 the T_1 starts to decrease with decreasing T in the region between −150 and −180°C. In TeF_6 the solid-solid phase transition apparently occurs before the maximum in T_1 is reached.

In all three compounds T_1 does not depend

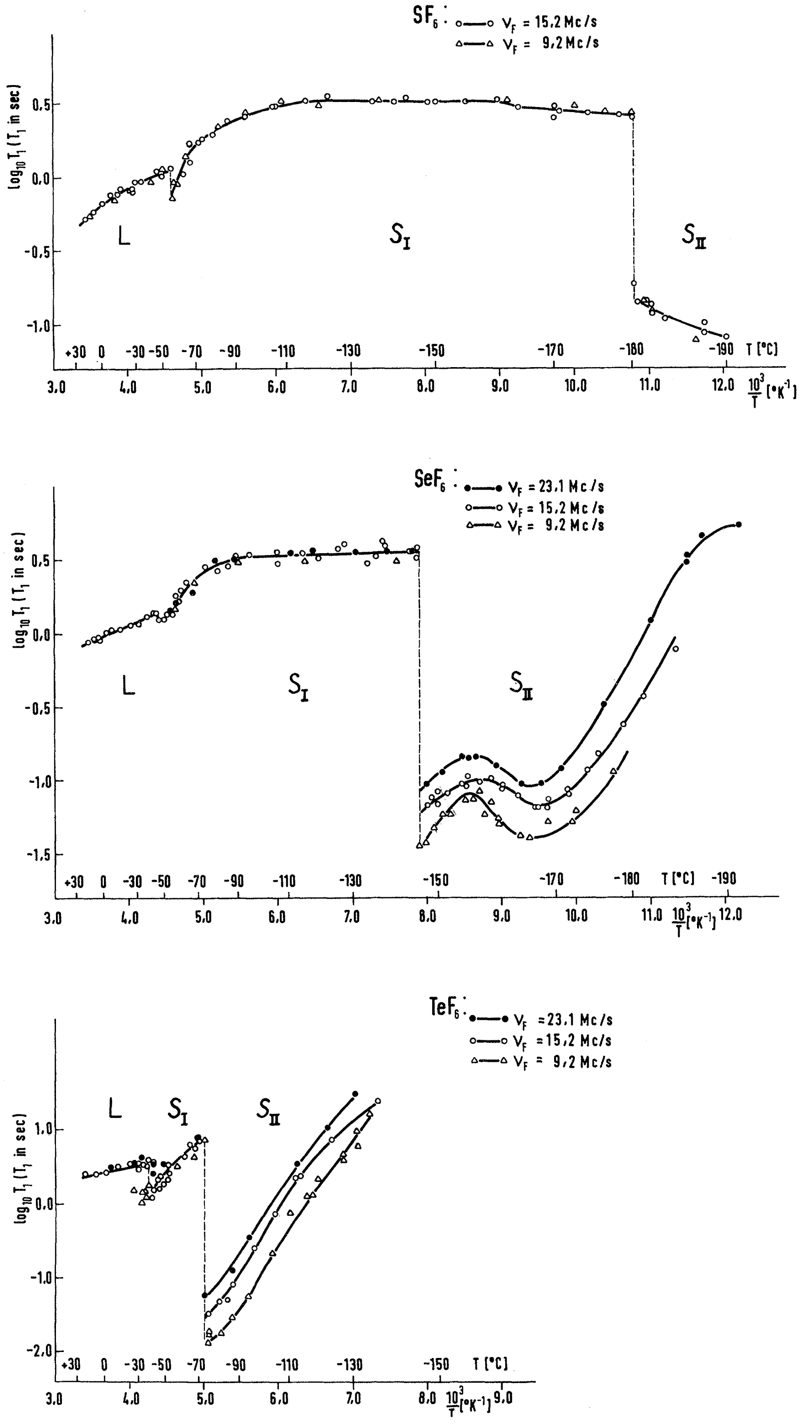

FIG. 1. Temperature dependences of the F^{19} spin-lattice relaxation times in SF_6, SeF_6, and TeF_6.

on frequency in this temperature region so that $\omega^2\tau_d^2 \ll 1$ (where τ_d is the correlation time governing the exponential time decay of the autocorrelation functions for molecular orientation and position). If dipolar interactions were to dominate the relaxation process, the condition $\omega^2\tau_d^2 \ll 1$ would lead to

$$(1/T_1)_d = C_1\tau_d; \tag{1}$$

and since

$$\tau_d = \tau_d^0 \exp(E_d/kT), \tag{2}$$

the relaxation time should decrease with decreasing temperature, contrary to observation. As will be shown later, the anisotropy of the chemical shift tensor $\Delta\delta$ is too small to contribute significantly to relaxation and since the longest T_1 observed in TeF_6 is 32 sec, whereas the maximum T_1 value in the solid phase I of this compound is 5 sec, paramagnetic impurities likewise cannot be responsible for the observed anomaly. The only plausible mechanism which remains appears to be the spin-rotation interaction.

Though no theory of spin-rotational relaxation exists as yet for solids, the similarity of the liquid and the solid-phase-I T_1 behavior suggests that, as in case of the BPP theory,[7] some features of the models originally developed for liquids can be transferred to disordered solids. The "transient rotation" model[4] of Gutowsky, where spin-rotational interactions are assumed to operate only when the molecule acquires enough energy to overcome the potential barrier and is actually rotating, as well as the "rotational diffusion" model of Hubbard,[5] both predict for $\omega^2\tau_d^2 \ll 1$ and spherical molecules a spin-rotational contribution to the relaxation time of the form

$$(1/T_1)_{\mathrm{SR}} = C_2/\tau_d, \tag{3}$$

so that the resulting expression for T_1,

$$T_1 = \frac{\tau_d}{C_2 + C_1(\tau_d)^2}, \tag{4}$$

as obtained from $(1/T_1) = (1/T_1)_d + (1/T_1)_{\mathrm{SR}}$, qualitatively reproduces the experimental plots of T_1 vs $10^3/T$ in solid phase I except at lowest temperatures where C_2 seems to become temperature dependent. Though one should not ascribe too much significance to the numerical values of the constants occurring in Eq. (4), it is perhaps worthwhile to mention that a typical value of τ_d at the T_1 maximum is 10^{-10} sec and of C_2, 10^{-11}. On going to solid phase II, τ_d discontinuously increases and dipolar interactions become rate determining for spin-lattice relaxation, as can be seen from the frequency dependence of T_1 and the occurrence of dipolar BPP minima. From the plots of $1/T_1$ versus the inverse square of the Larmor frequency, the anisotropy contribution to the relaxation rate can be determined. $\Delta\delta$ is found to be so small that it cannot influence relaxation in the T and frequency range considered.

The above results seem to throw new light on molecular reorientations and intermolecular interactions in disordered solids and open the possibility of studying correlation functions for the angular velocity of molecules not only in gases and liquids but also in the solid phase. Work along these lines is in progress.

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